



Visible-light-assisted aerobic photocatalytic oxidation of amines to imines over NH₂-MIL-125(Ti)



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ABSTRACT

NH₂-MIL-125(Ti), an amine-functionalized metal-organic-framework (MOF), was found for the first time to exhibit photocatalytic activity for the aerobic selective oxidation of amines to imines under visible light irradiations. Different amines can be effectively transformed to imines using O₂ over NH₂-MIL-125(Ti) under visible light irradiations. The photo-generated Ti³⁺ and ·O₂⁻ which was formed via the reaction between Ti³⁺ and O₂, are proposed to be involved in this transformation process based on the experimental observations and the ESR result. This work provides an economical, sustainable and green process for amines transformations and highlights the great potential of MOFs as photocatalysts for organic syntheses.

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1. Introduction

The selective oxidation of amines to the corresponding imines is one of the most important functional group transformations in organic chemistry since imines and their derivatives are important building blocks for the synthesis of fine chemicals and pharmaceuticals [1–6]. Traditionally, the formation of imine via dehydrating condensation of an amine with a carbonyl compound involves costly dehydrating reagents and sometimes the active nature of ketones or aldehydes can make this reaction difficult to control [7–9]. A more attractive strategy for the formation of imines is the direct oxidation of amines. However, oxidants such as N-tert-butylphenylsulfonimidoyl chloride or 2-iodoxybenzoic acid are always involved in some of the examined oxidation process, which is not so environmental friendly [10,11]. On the contrary, direct oxidation of amines to imines with molecular oxygen can afford an economical and green way for this transformation.

Metal-organic frameworks (MOFs) are a class of crystalline micro-mesoporous hybrid materials which have already shown a variety of applications [12–19]. The metal clusters building block, the inherent large surface areas, uniform but tunable cavities of MOFs and their tailor-able chemistry make them to be promising catalysts. Actually, recently there have been some reports that

demonstrated the applications of MOFs for aerobic selective oxidation of amines to imines [20,21]. For example, Garcia et al. reported that MIL-100(Fe) can selectively oxidize amines to imines with molecular oxygen [20]. Li et al. reported that this transformation can also be achieved over MOF-253 with a high efficiency using molecular oxygen as oxidant [21]. However, the aerobic oxidation of amines over all the examined MOF systems can occur only when heated. Therefore, it would be ideal if this transformation can be realized by means of photocatalysis since it is a more economical and green process. Actually photocatalysis is recently emerging as a promising strategy for organic transformations [22–24] and the selective oxidation of amines to imines by photocatalysis has already been realized in some semiconductor systems, like TiO₂, CdS, ZnIn₂S₄ and g-C₃N₄ [25–28]. Since previous studies have revealed that metal clusters in MOFs can be regarded as inorganic semiconductor quantum entities, while the organic linkers as antenna to activate these semiconductor quantum dots via the linker to metal cluster charge-transfer (LCCT) upon light excitation, it is believed that MOFs can also be promising photocatalysts [29]. Although studies on the photocatalysis based on MOFs is still in its infancy stage, the applications of MOFs in photocatalytic CO₂ and hydrogen evolutions have already been demonstrated [30–32]. However, there is still no report on the aerobic selective photocatalytic oxidation of amines over MOFs.

Our previous work has shown that NH₂-MIL-125(Ti) can photocatalytically reduce CO₂ to form formate under visible light [30]. To expand the application of NH₂-MIL-125(Ti) for other organic

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transformations, herein we study its photocatalytic performance for the aerobic oxidation of amine to imine. It was found that different amines can be effectively transformed to imines using O_2 over NH_2 -MIL-125(Ti) under visible light irradiations. This work provides an economical, sustainable and thus green process for the amine transformation and highlights the great potential of MOFs as photocatalysts for organic synthesis.

2. Experimental

2.1. Materials

2-aminoterephthalate (H_2ATA) were purchased from Alfa Aesar Co. Tetra-*n*-butyl titanate $Ti(OC_4H_9)_4$ were purchased from Shanghai Chemical Reagent Co. Anhydrous N,N -dimethylformamide (DMF) and methanol (MeOH) was purchased from Sigma Aldrich Co. All the reagents were analytical grade and used without further purifications.

2.2. Synthesis of NH_2 -MIL-125(Ti)

NH_2 -MIL-125(Ti) was synthesized following our previous reported procedure. 2-aminoterephthalic acid (H_2ATA) (1.36 g, 7.5 mmol) and $Ti(OC_4H_9)_4$ (1.8 ml, 5.3 mmol) were added into a solution containing DMF (9 ml) and dry MeOH (1 ml). The above mixture was stirred at room temperature for 30 min and was transferred to a 50 ml Teflon liner and heated at $150^\circ C$ for 72 h. After reaction, the resultant suspension was filtered, washed with DMF and MeOH respectively, extracted by Soxhlet extractor with MeOH and dried to obtain the bright yellow solid product.

2.3. Characterizations

X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with $Cu K\alpha$ radiation. The accelerating voltage and the applied current were 40 KV and 40 mA, respectively. Data were recorded at a scanning rate of $0.02^\circ 2\theta s^{-1}$ in the 2θ range of 5° – 60° . UV–visible diffuse reflectance spectra (UV–DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA). $BaSO_4$ was used as a reflectance standard in the UV–visible diffuse reflectance experiment. BET surface area was carried out on an ASAP2020M apparatus (Micromeritics Instrument Corp., USA). The samples were degassed in vacuum at $200^\circ C$ for 12 h and then measured at 77 K.

2.4. Photocatalytic reaction

The photocatalytic amine oxidation was performed in a sealed reaction tube pre-saturated with O_2 atmosphere under visible light irradiations. The photocatalyst (5 mg) suspended in solvent (2 ml) with amines (0.1 mmol) were degassed and saturated with O_2 before the photocatalytic reaction. The reaction was performed under the irradiation of a 300 W Xe lamp with a UV-cut filter to remove all wavelengths less than 420 nm and an IR-cut filter to remove all wavelengths larger than 800 nm. The reaction products were analyzed using a GC-FID (Shimadzu GC-2014) with a RTX-5 capillary column.

3. Results and discussion

NH_2 -MIL-125(Ti) was synthesized following the procedures reported previously [30]. The good agreement between the XRD patterns of the as-obtained product and the calculated NH_2 -MIL-125(Ti) indicated the formation of pure phase of NH_2 -MIL-125(Ti)

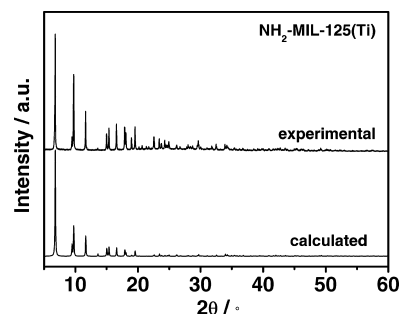


Fig. 1. XRD patterns of experimental and calculated NH_2 -MIL-125(Ti).

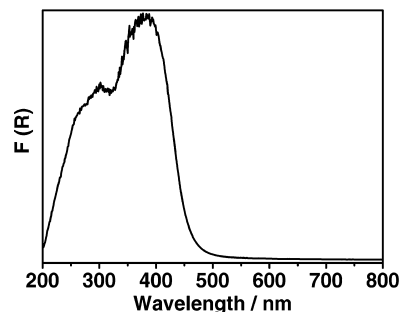


Fig. 2. DRS spectrum of NH_2 -MIL-125(Ti).

(Fig. 1). The BET specific surface area of the as-prepared NH_2 -MIL-125(Ti) ($1300 m^2 g^{-1}$) is slightly higher than that reported previously ($1203 m^2 g^{-1}$), indicating that NH_2 -MIL-125(Ti) with high quality was obtained [33]. The UV/visible diffuse reflectance spectra (DRS) of the as-prepared NH_2 -MIL-125(Ti) showed two absorption edges at about 350 nm and 550 nm, corresponding to the absorption of Ti–O oxo-clusters and the ligand-based absorption, respectively (Fig. 2).

To study the photocatalytic performance of NH_2 -MIL-125(Ti) for the aerobic amine oxidation, benzylamine was first selected as the substrate and the results were shown in Table 1. It was found that benzylamine can be converted to *N*-benzylidene benzylamine with a medium conversion (53%–73%) and high selectivity (70%–94%) in a variety of solvents after 12 h irradiations (Table 1, entry 1–4). Benzaldehyde and benzaldehyde were produced as the byproducts in these reactions. The solvent did show influence on the reaction. Acetonitrile (CH_3CN) was found to be the optimum medium among the solvents examined, which showed the best conversion

Table 1

Aerobic photocatalytic oxidation of benzylamine to *N*-benzylidene benzylamine over NH_2 -MIL-125(Ti) under various conditions.

Entry	Solvent	Conv. / %	Select. / %
1	CH_3CN	73	86
2	$ArCF_3$	57	94
3	DMF	67	70
4	Toluene	53	82
5 ^a	CH_3CN	–	–
6 ^b	CH_3CN	–	–
7 ^c	CH_3CN	73	86

^a The reaction was performed in dark.

^b The reaction was performed without photocatalyst.

^c The reaction continued after the photocatalyst was filtrated after 12 h irradiation.

Reaction conditions: 0.1 mmol of substrates, 5 mg NH_2 -MIL-125(Ti), solvent (2.0 mL), O_2 , irradiated for 12 h.

Table 2
Aerobic photocatalytic oxidation of various amines over NH₂-MIL-125(Ti).

Entry	Substrate	Product	Conv/ %	Select/ %
1			73	86
2			41	81
3			44	78
4			70	87
5			75	90
6			78	90
7			92	93
8			68	78
9			79	45
10		–	0	–
11 ^a			> 99	77

^a The reaction was performed without using a cut-off filter.

Reaction conditions: 0.1 mmol of substrates, 5 mg NH₂-MIL-125(Ti), CH₃CN (2.0 mL), O₂, visible light irradiation for 12 h.

of benzylamine (73%) and a relative high selectivity towards N-benzylidene benzylamine (86%) after 12 h irradiations (Table 1, entry 1). Therefore, CH₃CN was chosen as the reaction medium in the following studies. No detectable products can be obtained in absence of light or NH₂-MIL-125(Ti), indicating that the transformation of benzylamine to N-benzylidene benzylamine is truly induced by NH₂-MIL-125(Ti) photocatalysis (Table 1, entries 5 and 6).

No further oxidation occurred in the filtrate after the solid photocatalyst was removed from the reaction system after 12 h irradiations, suggesting that the amine transformation was truly induced by the heterogeneous photocatalysis of NH₂-MIL-125(Ti) (Table 1, entry 7). NH₂-MIL-125(Ti) after the photocatalytic reaction showed similar XRD patterns as that of the fresh one and the recycling use of the photocatalyst for three runs showed no obvious decrease of the photocatalytic activity, suggesting that the photocatalyst is stable during the amine oxidation reaction (Figs. 3 and 4).

The substrate scope of the aerobic oxidation of amines over NH₂-MIL-125(Ti) was also investigated and the results were shown in Table 2. Although the selective aerobic oxidation of all the benzylamine derivatives to their corresponding imines can proceed under the reaction conditions, the different substituents on the phenyl ring can influence the conversion rate and the selectivity, indicating the existence of an electronic effect (Table 2, entry 2–7). As compared with bare benzylamine, amines with electron withdrawing substituents on the phenyl ring exhibited decreased conversion (41%–44%) and selectivity (77%–81%), while that bearing electron donating ones showed enhanced conversion (75%–92%) and improved selectivity (90%–93%), with the exception observed over methyl substituted benzylamine, which exhibited a comparable conversion at 70%. This is probably due to the existence of the steric hindrance since benzylamine with methoxy (OCH₃) substituted at different position of phenyl ring showed reaction rate in the order of para- < meta- < orth- substituted. (Table 2, entry

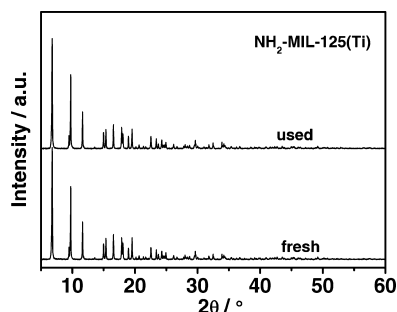


Fig. 3. The XRD patterns of $\text{NH}_2\text{-MIL-125(Ti)}$ before and after photocatalytic amine oxidation.

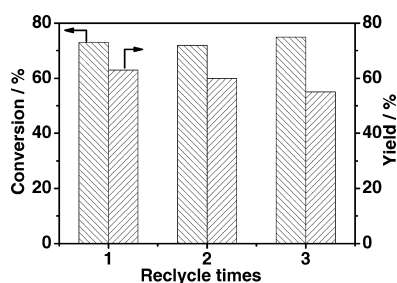


Fig. 4. Recycling test on $\text{NH}_2\text{-MIL-125(Ti)}$ for aerobic photocatalytic oxidation of benzylamine under visible light irradiations.

5–7). Secondary amines also afforded the corresponding imines with comparable conversion (68%) and selectivity (78%) over $\text{NH}_2\text{-MIL-125(Ti)}$ (Table 2, entry 8). In addition to the aromatic amines, heterocyclic amines can also be oxidized to dehydrogenated imines but the selectivity was lower than that of benzylic homologues (Table 2, entry 9). No oxidation occurred for amine lacking hydrogen at the α -carbon, suggesting the involvement of α -hydrogen in the imines formation (Table 2, entry 10).

It is generally believed that the aerobic oxidation of amines to imines proceeds via an oxygenation pathway, in which the in-situ formed superoxide radical anion ($\cdot\text{O}_2^-$) plays an important role [26]. Our previous work on photocatalytic CO_2 reduction over $\text{NH}_2\text{-MIL-125(Ti)}$ revealed that upon irradiations, an electron transferred from the excited ligand to the Ti-O oxo-clusters (LMCT) to form Ti^{3+} is responsible for CO_2 reduction to form HCOO^- [30]. It was proposed that Ti^{3+} is also involved in the aerobic oxidation of amines to imines over $\text{NH}_2\text{-MIL-125(Ti)}$. As shown in Fig. 5, a color change from the original yellow to green was observed when the close system containing the suspension of $\text{NH}_2\text{-MIL-125(Ti)}$ and benzylamines in CH_3CN was irradiated with visible light, indicating the formation of the Ti^{3+} moiety. The introduction of O_2 into the reaction system change the color back to yellow, suggesting that the

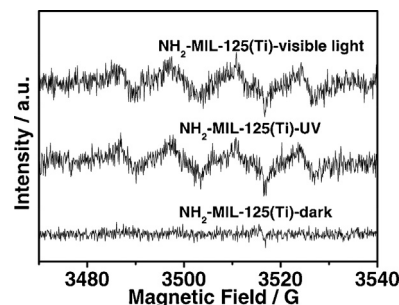
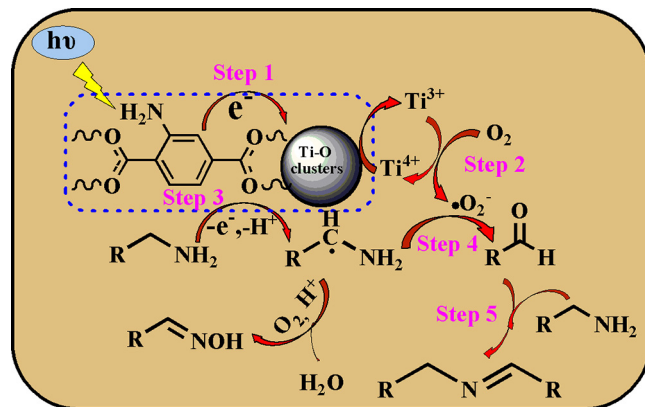


Fig. 6. DMPO spin-trapping ESR spectra of $\text{NH}_2\text{-MIL-125(Ti)}$ in methanol dispersion in dark, under UV and visible light irradiations.



Scheme 1. Proposed mechanism of the photocatalytic amines oxidation over $\text{NH}_2\text{-MIL-125(Ti)}$.

as-formed Ti^{3+} was oxidized back to Ti^{4+} by O_2 to form $\cdot\text{O}_2^-$. Actually, the capability to form $\cdot\text{O}_2^-$ over irradiated $\text{NH}_2\text{-MIL-125(Ti)}$ was confirmed by the ESR result (Fig. 6). No signal was observed when the $\text{NH}_2\text{-MIL-125(Ti)}$ suspension was in dark. After irradiations, signal for DMPO- $\cdot\text{O}_2^-$ adduct was found, indicating that $\text{NH}_2\text{-MIL-125(Ti)}$ is capable to reduce O_2 to $\cdot\text{O}_2^-$. Therefore, a possible mechanism for the amines oxidation to imines was proposed based on these observations (Scheme 1). Upon irradiations, the excited ligand ATA can transfer an electron to Ti-O oxo-clusters to form Ti^{3+} moiety. (step 1 in Scheme 1). The as-formed Ti^{3+} can react with molecular oxygen to generate $\cdot\text{O}_2^-$ while Ti^{3+} was oxidized back to Ti^{4+} (step 2 in Scheme 1). In the meantime, amines can donate an electron, followed by a de-protonation process to generate the carbon centered radical (step 3 in Scheme 1). In fact, the use of amines as an electron donor has been well documented in the previous reports. The interaction between the photo-generated carbon centered radical and the $\cdot\text{O}_2^-$ will lead to the formation of aldehydes (step 4 in Scheme 1). The nucleophilic attack on aldehydes by the un-reacted amines will thus yield the correspond-

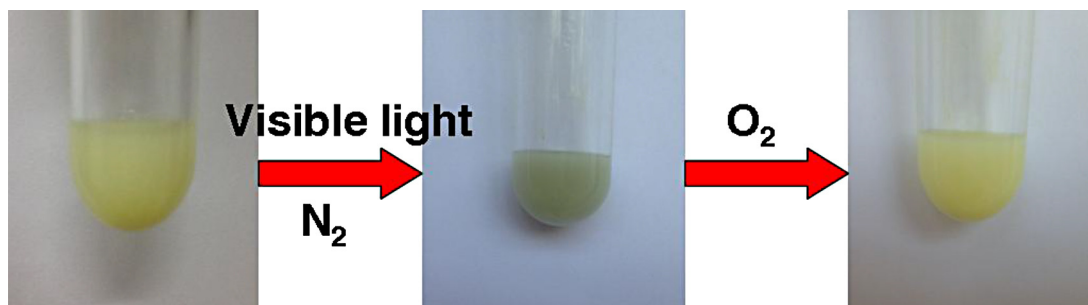


Fig. 5. Photographs of the suspension of $\text{NH}_2\text{-MIL-125(Ti)}$ and amines during the photocatalytic reaction.

ing imines via dehydration (step 5 in Scheme 1). A small amount of the byproduct benzaldoxime is probably generated via the reaction between carbon center radical with molecular oxygen, followed by a dehydration process [34].

Based on the above mechanism, Ti^{3+} is involved in the amine oxidation. Since Ti^{3+} can also be generated via the direct excitation of Ti–O cluster under UV irradiations in addition to the LMCT under visible light irradiations, it is believed that the photocatalytic efficiency can be further improved by a simultaneous irradiation with UV and visible light (Fig. 6). Actually, the reaction carried out without using a cut-off filter did show enhanced performance. The conversion of benzylamine was >99% after 12 h irradiation, higher than that performed under visible light (73%) (Table 2, entry 11).

4. Conclusions

In summary, a selective photocatalytic oxidation of amines to imines using molecular oxygen as oxidant was achieved over NH_2 -MIL-125(Ti) under visible light irradiations. This work provides an economical, sustainable and thus green process for the amine transformation. Although the performance for the oxidation of amines over the current NH_2 -MIL-125(Ti) still has a large space to improve, this study still highlights the great potential of MOFs as photocatalysts for organic synthesis as considering the versatile MOF structure already been developed.

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